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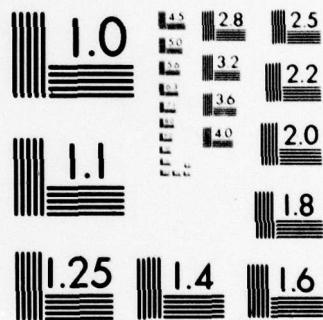
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PHYSICOCHEMICAL STUDIES OF SOLUTES IN MICROEMULSIONS

by

10 Raymond A. Mackay  
Associate Professor  
Department of Chemistry  
Drexel University  
Philadelphia, PA 19104

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  We have investigated the utility of oil in water microemulsions as media for the study of processes occurring at microscopic oil/ water interfaces. Various microemulsion systems using emulsifiers of the surfactant/alcohol type have been formulated. Cationic, anionic, and nonionic surfactants have been employed, and phase maps for seven of these systems have been obtained. Selected systems		



have been further characterized by conductance, dye, and light scattering measurements. Electrochemical studies consisting of specific ion electrode, polarographic and conductivity measurements have been performed, and quantitative expressions for the transport properties of ions in the nonionic microemulsions have been developed. Acid-base equilibria employing indicators have shown the usefulness of average pH values as determined by glass electrode data.

The reactions of phosphate ester with hydroxide and fluoride in cationic and mixed cationic/nonionic microemulsions show that the intrinsic rate constant ( $k_i$ ) higher than in aqueous cationic micelles. The use of small added amounts of functionalized surfactant yields a rate increase of almost two orders of magnitude in cationic microemulsion. The results of this study clearly indicate the utility of microemulsion media both for fundamental studies and for application to problems such as solubilization, catalysis, and chemical decontamination.

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### FOREWORD

This is the final report on grant DAAG29-76G-0174, "Physico-chemical Studies of Solutes in Microemulsions", covering the period April 1, 1976, to April 30, 1979. Much of the work performed during this period is published, in press, or in preparation. This report will therefore consist of a summary of the work performed with references to the published or in press material, supplemented by as yet unpublished or incomplete data where appropriate.

## TABLE OF CONTENTS

Report Documentation Page	ii
Foreword	iv
List of Tables	vi
List of Figures	vii
I. Introduction	1
II. Results	
A. Systems	3
B. Electrochemical Measurements	9
C. Interactions and Reactions	16
III. Summary	24
IV. Bibliography	26



List of Tables:

- Table 1. Microemulsion systems for which phase maps are available.
- Table 2. Microemulsion compositions.
- Table 3. The difference in potential at 25 degrees C between saturated solutions of various salts in a nonionic o/w microemulsion using a flouride ion specific elctrode.
- Table 4. Phase volumes obtained from flouride ion electrode measurements in a nonionic mineral oil in water microemulsion.
- Table 5. pKa values for Chlorophenol Red in various microemulsion systems.
- Table 6. Rate constants for reaction of p-nitrophenylphosphate with hydroxide and flouride in a CTAB/butanol/hexadecane o/w microemulsion at 25 degrees C.



LIST OF FIGURES:

- Figure 1. A model of an oil droplet in an o/w micellar emulsion stabilized by ionic detergent and an alcohol.
- Figure 2. Pseudo three component phase map of the emulsifier E (56.5% N-Butanol, 43.5% Olin J300 nonionic surfactant, w/w), water W and tributylphosphate as oil O.
- Figure 3. Pseudo three component phase map of the water/mineral oil/N-pentanol/tween 40 system.
- Figure 4. Pseudo three component phase map of the CTAB/butanol/hexadecane/water system.
- Figure 5. The equivalent conductance of a water/benzene/CPB/cyclohexanol microemulsion and a water/mineral oil/SCS/n-pentanol microemulsion.
- Figure 6. Glass electrode pH of microemulsion vs pH of aqueous buffer used to form it.
- Figure 7. Effect of mixed CTAB/B200 microemulsions on reaction of p-nitrophenyl diphenylphosphate with nucleophile.

## I. INTRODUCTION:

The purpose of this study was to investigate the utility of oil in water (o/w) microemulsion systems for studies of interactions at microscopic oil water interfaces and for possible applications to areas such as solubilization decontamination.

All of the microemulsions employed in this study are transparent, isotropic fluids consisting of four components and containing relatively high amounts of emulsifier (10-40%). The emulsifier E will normally consist of a surfactant S and alcohol A. The aqueous component W may be pure water or may contain added salts or buffers. The oil O can be any liquid which is not miscible with water such as benzene, hexane, carbon tetrachloride, mineral oil, etc. In addition to being mechanically stable, all of these microemulsions appear to be thermodynamically stable as well. Some of the criteria which they meet are listed below.

1. Their formation is spontaneous and independent of the method or order of addition of components.
2. The value of any physical measurement (e.g. conductivity) at a given composition is independent of the path by which that composition is reached.
3. After being subjected to a perturbation which causes phase separation (e.g. temperature) the system returns to its original state. Thus, their internal structure may be described as a collection of oil microdroplets dispersed in water. The volume occupied by the dispersed phase (phase volume) is high (e.g. 20-80%). The droplet diameter is on the order of 100-600Å, and in this size range has been found to be monodisperse. The droplet itself may be conceptually divided into two regions, the oil core and the surface or interphase region. Essentially all of the surfactant and a part of the alcohol cosurfactant is located in the interphase region. A model of an o/w micellar emulsion droplet stabilized by an ionic detergent and an alcohol is shown in Figure 1.

The results of this study are interrelated to varying extents. However, for convenience the report is divided into three sections consisting of (1) systems, (2) electrochemical measurements, and (3) interactions and reactions. The first section will include a discussion of the microemulsion employed, phase maps, physical characteristics and solubility. The second section will contain the results of conductivity, pH, specific ion electrode and polarographic measurements. The third section will deal with indicator and reaction studies, particularly phosphate ester hydrolysis.



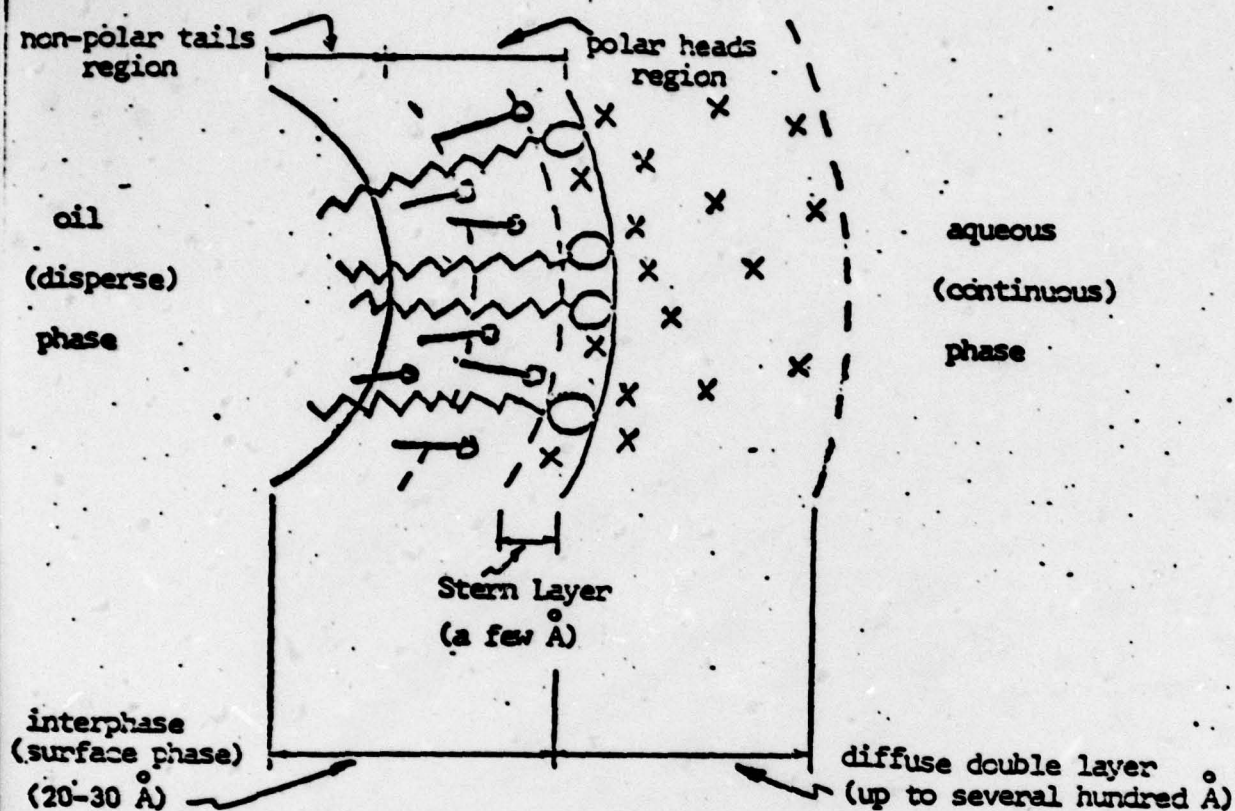


Figure 1. A model of an oil microdroplet in an O/W micellar emulsion stabilized by ionic detergent and an alcohol ( $C_{12}$ ). The counterions ( $\times$ ), head groups ( $\odot$ ), hydrocarbon chains ( $\sim$ ) and alcohol molecules ( $\text{—}\bullet$ ) are schematically indicated to denote their relative locations but not their number, distribution or configuration. Some alcohol is normally present in the oil phase, and both oil and water molecules can penetrate the interphase to some extent.

## II. RESULTS:

A. Systems: A large number of systems consisting of emulsifier E (mixture of surfactant S and alcohol A), oil O and water W have been examined. Since there are four components, the clear, isotropic single phase regions are represented using psuedo three component phase maps such as that shown in Figure 2. All compositions are given by weight. It should be understood that the clear area labelled C is most likely to contain two or more different phases. For example, the region bordering the E-W line at higher water content (probably above 30%) is the o/w microemulsion region, although there may even be more structural change in the "peninsula" on this area. The long thin spike extending toward the O apex has not been investigated but likely represents a w/o type system.



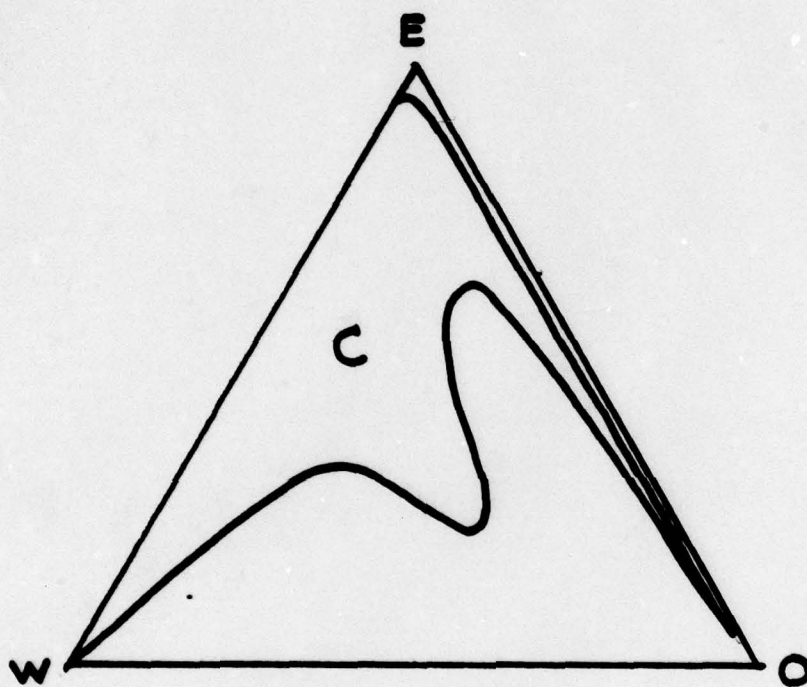


FIGURE 2: Pseudo three component phase map of emulsifier E (56.5% N-butanol, 43.5% Olin J300 nonionic surfactant, w/w), water W and tributylphosphate as oil O. The area C is a clear, isotropic phase region.

In this study, the alcohol A was normally either N-butanol or N-pentanol, and the oil either mineral oil or more commonly hexadecane. A few systems employing tributylphosphate as the oil were also examined. The anionic surfactant S was sodium cetyl sulfate (SCS), the cationic surfactant cetyltrimethylammonium bromide (CTAB), and various nonionic surfactants. These were mostly commercial mixtures (e.g. Tween 40 and Tween 60 from ICI America, Inc., or B200 and J300 from Olin Corp.), although a single component nonionic, polyoxethylene 10 oleyl ether (Brij 96) was also employed and found to be generally the most satisfactory. The phase maps were obtained by titrating an initial composition on the E-O axis with water to clear and turbid endpoints. Similar titrations were performed starting with compositions on the E-W axis and adding oil. A summary of the major systems employed and the references to them are given in Table 1. The phase map of the tween 40 system is also given in Figure 3 since the paper containing it has only just been submitted for publication. Two categories are given: phase maps and compositions. The former has already been discussed (vide supra) and the latter refers to ranges of compositions which were employed but for which the complete phase map was not determined. These are given in Table 2.

The droplet diameters in these o/w microemulsion systems remain approximately constant upon dilution with water and increase exponentially upon addition of oil as indicated by our light scattering measurements (5). Over the range of compositions normally employed, drop diameters are generally on the order of 80-180Å.

The ionic surfactants can be purified by recrystallization, generally from methanol (6). However, the commercial nonionic surfactants have been found to contain large amounts of ionic impurities, as well as some organic ones. The ionic impurities appear to contain, among other things, a weak acid and its salt. These impurities have been found to interfere not only with electrode measurements, but also with

TABLE 1. Microemulsion systems for which phase maps are available.

Surfactant <sup>a</sup> / alcohol <sup>b</sup> / oil <sup>c</sup>			Reference
SCS	/ PA	/ MO	2
Tween 60	/ PA	/ HD	3
CTAB	/ BA	/ HD	4
Brij 96	/ BA	/ HD	5
Tween 40	/ PA	/ MO	6

a. Sodium cetyl sulfate (SCS), cetyltrimethylammonium bromide (CTAB).

b. n-butanol (BA), n-pentanol (PA).

c. heavy mineral oil, Nujol (MO), hexadecane (HD)



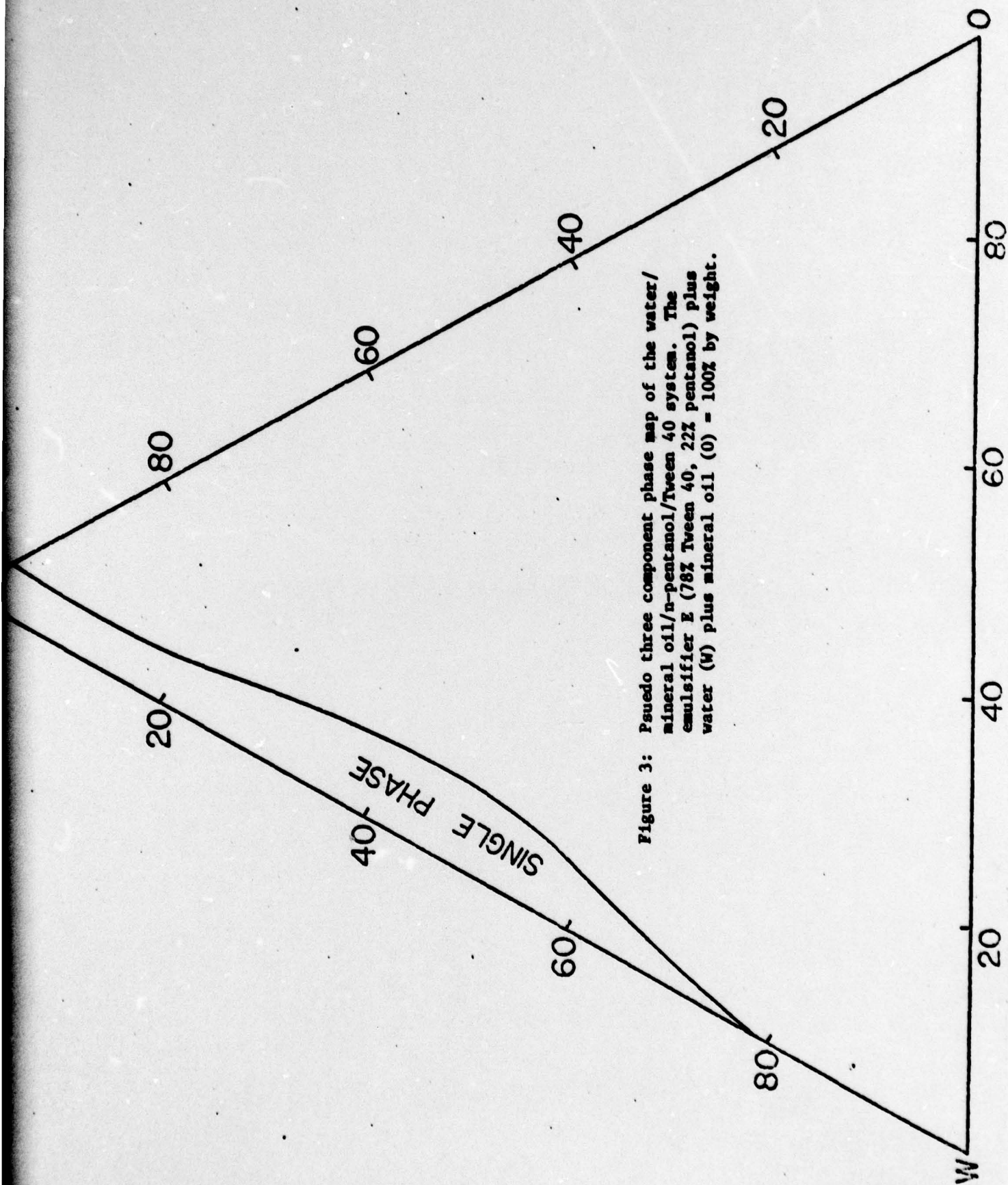


Figure 3: Pseudo three component phase map of the water/mineral oil/n-pentanol/Tween 40 system. The emulsifier E (78% Tween 40, 22% pentanol) plus water (W) plus mineral oil (O) = 100% by weight.



TABLE 2. Microemulsion Compositions

Surfactant <sup>a</sup>	Alcohol <sup>b</sup>	Oil <sup>c</sup>	Reference
Tween 60, Tween 81	PA	MO	1
Tween 60, Span 80	PA	MO	2
CPB, CTAB	PA	MO	2
CPB	CHA	benzene	2
PO	CHA	benzene	2
Tween 60	PA	MO	3
Tween 60, Tween 81	PA	HD	3
B200	BA	HD	6
J300	BA	HD	6

a. Cetylpyridinium bromide (CPB), Potassium oleate (PO), nonionic Tween and Span from ICI America, B200 and J300 from Olin Corp.

See also Table 1.

b. Cyclohexanol (CHA), see also Table 1.

c. See Table 1.

reaction studies. They may be removed to a satisfactory level by careful neutralization of the acid with NaOH followed by deionization of the microemulsion with mixed bed ion exchange resin (6). The resin should be washed well with water, drained, and used "internally" wet. The deionization should be followed conductimetrically since over-treatment is undesirable. The optimum stirring time depends on water content, but is generally on the order of an hour.

Finally, some comments on solubility are in order. Most oils require large amounts of emulsifier to solubilize (in our o/w type systems) more than about 30% oil at any emulsifier concentration. However, when tributylphosphate is used as the oil in a CTAB/butanol system, an enormous clear area results as shown in Figure 4. Preliminary conductivity measurements indicate the existence of at least three different regions, as yet unidentified. Since mixed microemulsion systems of the ionic/nonionic type are usually miscible in all proportions, the proper solute (e.g. a phosphate ester) can be solubilized in a microemulsion containing another oil (e.g. hexadecane) in very large quantity.

B. Electrochemical Measurements: These studies consist of potentiometric (specific ion electrode), conductometric and polarographic measurements. The former were initiated to monitor effective electrolyte concentration and buffer pH in nonionic systems, and then to extend them to anionic and cationic systems in which stronger ion binding is present. The latter were intended to explore the transport properties of ionic solutes in microemulsions, and to serve as an adjunct to ion binding studies.

In nonionic o/w systems, we have achieved a good semi-empirical

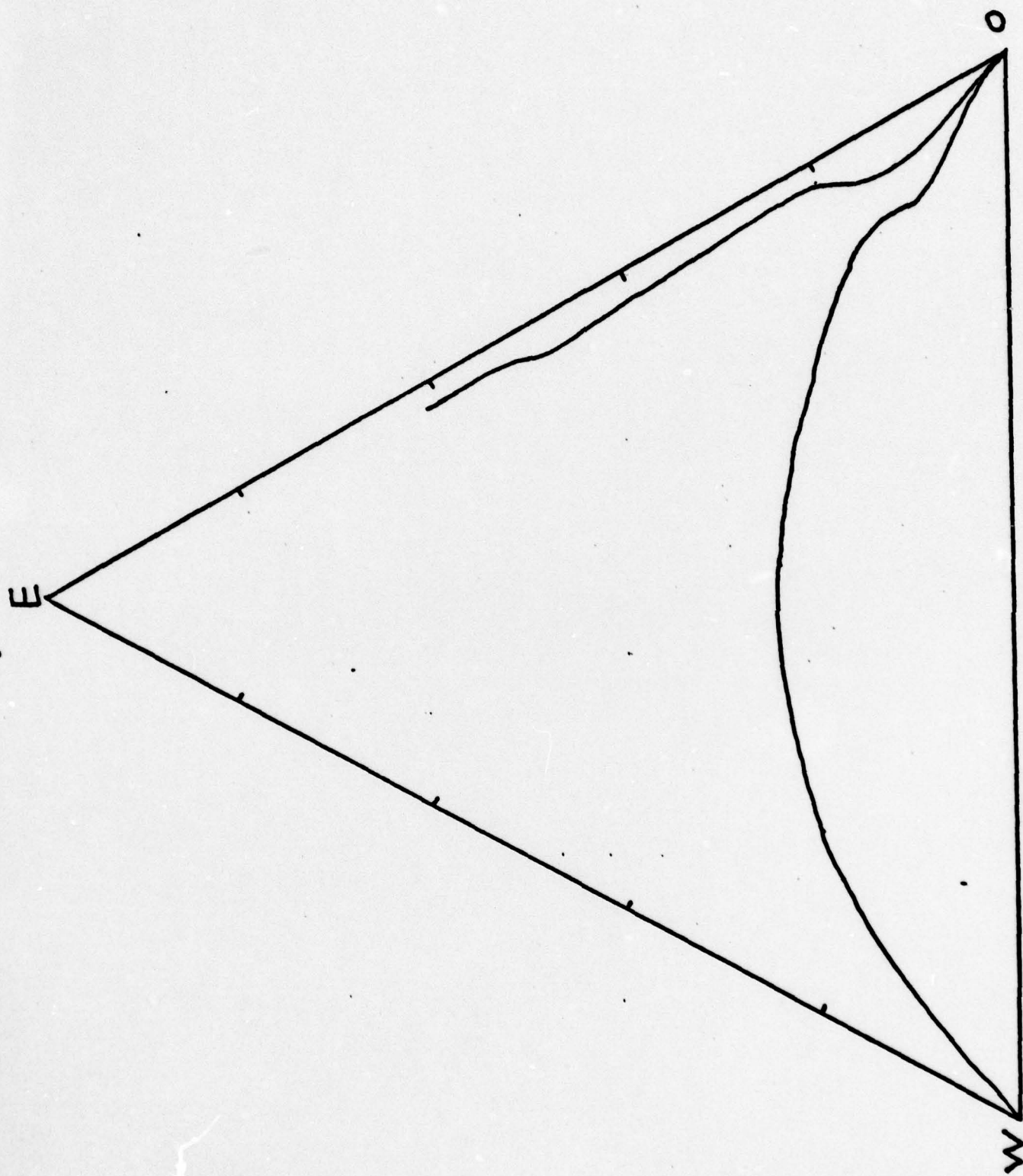


FIGURE 4j. Psuedo three component phase map of the CTAB/BUTANOL/HEXADECANE/water system. (E = 50/50 wt. percent CTAB/BUTANOL, O = TRIBUTYL PHOSPHATE, W = Water).



understanding of the transport properties of ions (3). The equivalent conductance ( $\Lambda$ ) of a salt added to a coarse emulsion generally fits an equation of the form  $\Lambda/\Lambda_0 = (1-\phi)^{0.5}$ , where  $\Lambda$  and  $\Lambda_0$  are the values in the emulsion of phase volume  $\phi$  and pure water, respectively. In microemulsion systems of low oil content, we find an exponent of 1.5 rather than 0.5. Assuming the validity of Stoke's law, a relationship for the diffusion coefficient ( $D$ ) of a solute species may be derived which has the form  $D/D_0 = (1-\phi)^{2.5}$ . This has been experimentally verified by means of polarography. Identical results are obtained for cadmium (II) at a dropping mercury electrode and both ferri and ferrocyanide at a rotating platinum electrode in a variety of nonionic microemulsions.

When the oil content is increased, the exponent decreases. We have shown that the decrease in  $N$  varies linearly with increasing droplet diameter (5), indicating that the droplet concentration varies continuously with oil content as opposed to the previously postulated abrupt change (3).

Conductivity and polarographic measurements have been extended to ionic microemulsions, but a quantitative interpretation of the data has not yet been achieved. Upon dilution with water, all ionic o/w systems studied exhibit the behavior shown in figure 5 (2). The diffusion coefficients of Cd(II) in an anionic microemulsion also quantitatively follow the conductance curve. If, as might be expected, the cadmium ion is strongly bound to the (net) negatively charged drop, this behavior should not be obtained. Additional preliminary data on other ions in both anionic and cationic micellar emulsions have been obtained, but no clear interpretation can be given at present. However, it appears that the transport of species bound to a drop is controlled by the dissociation of the species from the drop and its subsequent diffusion to another drop.

Specific ion electrode measurements involving  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{F}^-$ , and  $\text{H}^+$  have been made in a variety of nonionic o/w microemulsions (1).



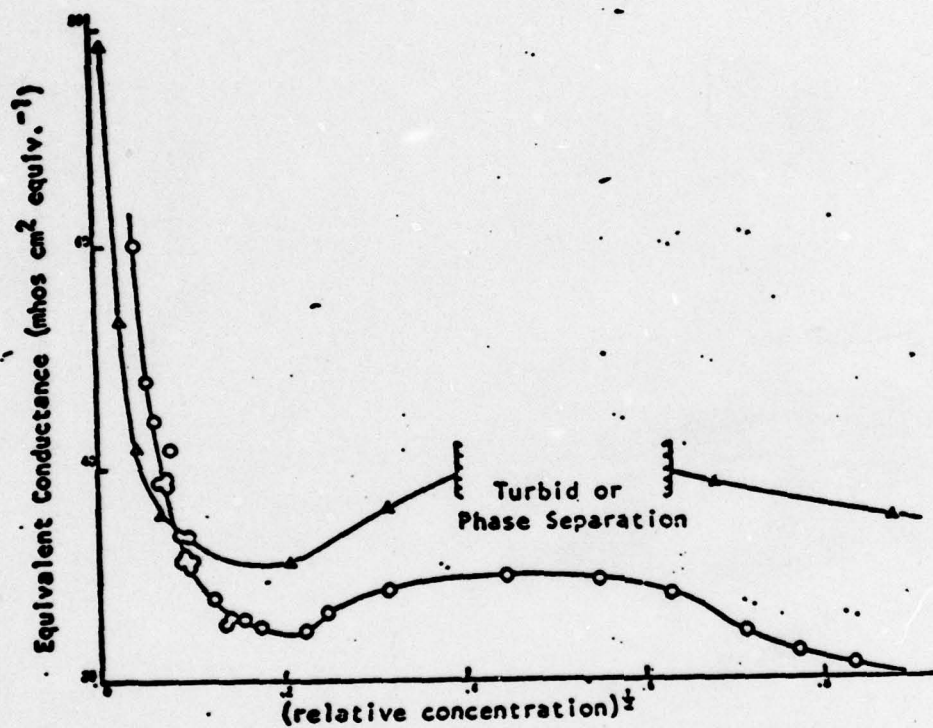


Figure 5 The equivalent conductance of a water/benzene/CPS/cyclohexanol microemulsion (O-O) and a water/mineral oil/SCS/n-pentanol microemulsion (Δ-Δ). The undiluted microemulsion, which is .5% in CPS or in the case of SCS, .35M, is given a relative concentration of 1.0.

Using the most naive approach, it might be expected that the overall (stoichiometric) concentration of a simple aqueous ion  $(X)_m$  be given by

$$(X)_m = (X)_0 / (1-\theta) \quad (1)$$

Values of  $\theta$  obtained from this equation are reproducible, but consistently low. There are clearly liquid junction and solvent (assymetry) effects on the electrodes. This does not preclude use of the electrodes in nonionic systems since calibration curves can be employed. It is always necessary to check the effect of both total salt concentration and nature of counterion since this can have an effect on microemulsion stability. However, without a method for correcting the electrode response, measurements in ionic systems cannot be made. We have attempted to perform such a correction by employing a saturated solution of a sparingly soluble salt containing the ion of interest. These measurements have been conducted in nonionic systems where we effectively know the answer as a check on the method. The principal involved is that a saturated solution of the same salt in both pure water and in a microemulsion has the same activity, and should therefore elicit the same electrode response. Any difference in potential may thus be ascribed to junction and solvent effects. One example is the use of a fluoride specific ion electrode in a mineral oil in water microemulsion stabilized by Tween 40 and pentanol to which known amounts of NaF were added. The mV readings were transformed into effective fluoride concentrations using an aqueous calibration curve. Three salts of differing solubility ( $CaF_2$ ,  $BaF_2$  and  $PbF_2$ ) were employed to insure that the salt itself was not responsible for any observed effects. The agreement is at least fair, as shown in Table 3. Values of  $(1-\theta)$  calculated with and without the correction are given in Table 4. The corrected values represent averages of the three saturated salt solutions. There is a dramatic improvement, but it is still not of sufficient accuracy to permit its use as an independent correction factor. It is possible of course that similar measurements in ionic systems are generally less severe than on nonionic systems.

TABLE 3. The difference in potential\* at 25°C between saturated solutions of various salts in a nonionic o/w microemulsion and water using a fluoride ion specific electrode. (vide text).

$\text{XH}_2\text{O}$ (w/w)	$\text{BaF}_2$	$\text{CaF}_2$	$\text{PbF}_2$
20	108	121	119
30	85	90	93
40	60	64	66
50	41	44	45
60	24	27	29
70	17	18	18
80	10	10	11

\* The potential difference is given as water minus microemulsion, in mV.



TABLE 4. Phase volumes obtained from fluoride ion electrode measurements in a nonionic mineral oil in water microemulsion. (vide text).

comp. <sup>a</sup>	0.01M NaF <sup>b</sup>	corrected <sup>c</sup>
0.20	0.00	0.10
0.30	0.01	0.31
0.40	0.02	0.53
0.50	0.08	0.70
0.60	0.19	0.78
0.70	0.36	0.89
0.80	0.57	1.16

- a. Value of  $1-\phi$  calculated from composition;  $1-\phi = wg/$  where  $w$  is the weight fraction water and  $g$  is the specific gravity of the microemulsion.
- b. Calculated from eqn (1).
- c. Corrected using saturated salt solution.

Finally, we have recently initiated  $pK_a$  measurements of adsorbed indicator (chlorophenol red) in o/w microemulsions of all charge types, as an adjunct to these determinations, as well as for chemical reaction studies. Glass electrode pH measurements have been made in the buffered dispersions. Attempts have been made to control the adsorption of the buffer by employing only (+/++) and (-/--) charge types, since neutral buffer molecules such as acetic acid are solubilized by the microdroplet (2). Typical results are shown in Figure 6, and are reasonably independent of buffer concentration in the .01-.04M range. Microemulsions stabilized by nonionic surfactants are more susceptible to salt effects than those stabilized by ionic surfactants. There are not only solvent effects on the glass electrode, but effects caused by the specific buffer as well. For example, buffers with the same pH in water but of opposite charge type give different readings in the same microemulsion. Nonetheless, although the aqueous and microemulsion pH values themselves do not seem to be directly related to the actual pH, the average of the two yield self-consistent  $pK_a$  values. These will be discussed in the next section. Thus, it appears that the physically most meaningful quantity to employ in these media is the geometric mean of the aqueous and microemulsion hydrogen ion activities as determined by a glass electrode.

C. Interactions and Reactions: The two principal study areas consist of acid-base equilibria and reactions with nucleophiles.

The compound 1-methyl-4-cyanoformylpyridinium oximate (CPO) has been used to determine ion binding and buffer adsorption in the microemulsion systems (2). CPO is more soluble in water than in polar or nonpolar organic solvents, and is not taken up by aqueous ionic or nonionic micelles. The substance also possesses intramolecular charge-transfer bands which are very solvent sensitive and disappear upon protonation or complexation. If wavelength shifts of only a few nm are observed, the indicator is essentially located in the aqueous continuous phase. However, substantial wavelength shifts



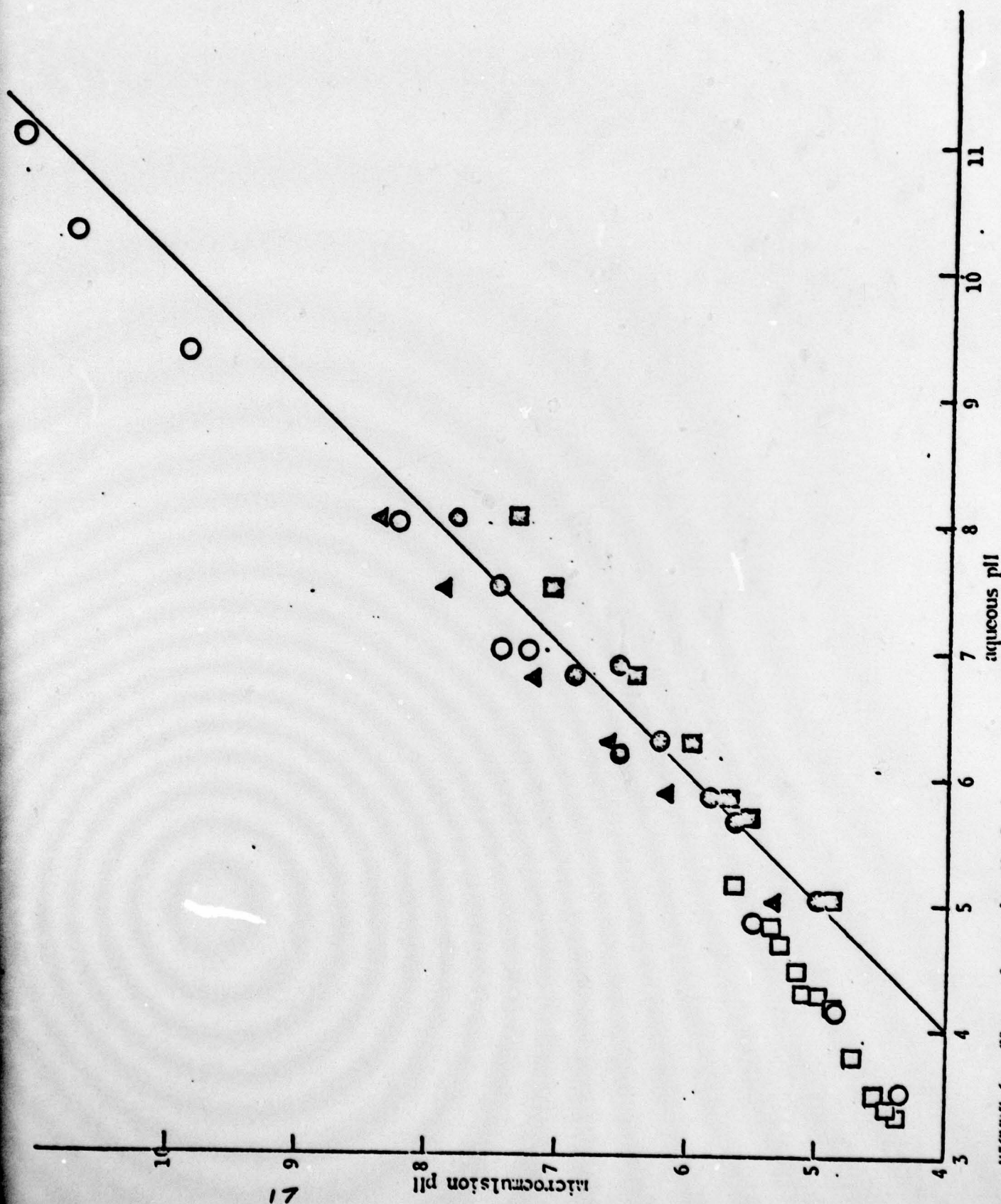


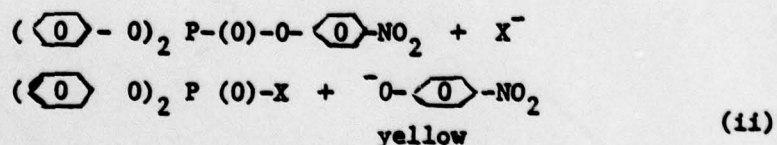
FIGURE 6. Glass electrode pH of microemulsion vs pH of aqueous buffer used to form it. All systems contain 50% buffer (aqueous buffer). Circles, 50% buffer; Triangles, 40% buffer; Squares, 30% buffer; Diamonds, 20% buffer.



indicate uptake by the droplet. In nonionic systems, the distribution ratio between the continuous and disperse phases can be estimated from the effective pKa. Thus, CPO is of limited utility in microemulsions, but can also be used to indicate possible phase boundaries. As a probe of the droplet microenvironment and pH, it can probably be utilized in the form of a 1-alkyl long chain derivative.

A number of pKa studies involving chlorophenol red have been carried out, as mentioned above. These have been quite useful in probing the dielectric constant and effective surface pH. The results of these studies (6) indicate that the interphase region of the microdroplet in which the dye is located has an effective dielectric constant of about 20, and that the intrinsic pKa of a dye is the same in all microemulsions of this type provided both indicator species are in the same average environment. The effective aqueous concentration of hydrogen ion is related to the geometric mean of aqueous buffer and microemulsion concentrations, as evidenced by the data in Table 5.

In order to examine the factors which control the rate of nucleophilic attack in the microdroplet o/w interface, we have investigated the reaction of oil soluble p-nitrophenyl-diphenylphosphate with aqueous fluoride and hydroxide. The reaction has previously been studied in both solution and aqueous cationic cetyltrimethyl ammonium bromide (CTAB) micelles. The rate in these cases is first order in both ester and nucleophile, and proceeds according to equation (ii), where  $X^- = F^-$  or  $OH^-$ .



In basic ( $\text{pH} \geq 9$ ) solution, the p-nitrophenol is fully ionized with an absorption maximum at 400nm. For  $X^- = OH^-$ , the product diphenylphosphoric acid is a strong acid and is fully ionized even at lower pH. In aqueous CTAB micelles, a maximum increase in the second order rate constant of about a factor a 30 over that in aqueous dioxane is observed.

Table 5.  $pK_a$  values for Chlorophenol Red in Various Microemulsion Systems.

System	Buffer <sup>a</sup>	$pK^b$	$pK_m^c$	$p\bar{K}^d$
A. 30% water, 0.04 M buffer, 19°C.				
CTAB	pip	6.29	6.57	6.4
CTAB/B200 <sup>e</sup>	pip			
75/25		6.50	6.61	6.6
50/50		6.62	6.73	6.7
25/75		6.74	6.98	6.9
B200	phos	7.23	7.88	7.6
	en	7.75	7.45	7.6
J300	phos	7.11	8.01	7.6
	en	8.10	7.83	8.0

B. 40% water, 0.10 M buffer, 25°C.

CTAB	pip	6.34	6.63	6.5
	phos	6.15	6.54	6.4
SCS	en	6.27	7.58	6.9
	phos	6.60	7.15	6.9
Brij 96	en	7.40	7.25	7.3
		6.90	7.45	7.2

a. Piperizine (pip), ethylenediamine (en) and phosphate (phos).

b. Calculated using pH of aqueous buffer ( $\pm 0.05$ ).

c. Calculated using pH of microemulsion ( $\pm 0.05$ ).

d.  $p\bar{K} = (pK + pK_m)/2$  ( $\pm 0.1$ ).

e. Mixture of CTAB and B200 microemulsion, each containing same weight percent total emulsifier and moles of surfactant, given as percent by volume.



To serve as a basis for comparison, we developed a hexadecane in water microemulsion stabilized by CTAB and butanol (Table 1). The reaction in the microemulsion was also found to be first order (to at least 75% completion) in both ester and nucleophile. Starting with 10% oil, the second order rate constants  $k_2$  were measured as a function of water content (4). Some results are given in Table 6. The values differ by at most a factor of two, neglecting the  $\phi = 0.79$  value. This composition is likely outside of the o/w microemulsion range. However, even this relatively small variation can be reduced substantially by correcting the values of  $k_2$  for the effective concentrations of reagents. Since the hydroxide is in the aqueous phase, its effective concentration is given by  $(OH^-)/(1-\phi)$ . Since the phosphate is located in the droplet, its effective concentration is proportional to (ester)/ $\phi$ . Thus, the volume corrected rate constant  $k_{2,v} = k_2 \phi(1-\phi)$ . The values of  $k_{2,v}$  are almost invariant within experimental error ( $\pm 5\%$ ). If the ester is concentrated in a thin surface layer of the drop and if the radius does not change upon dilution, then the same correction factor holds. If the radius does change (decrease) so as to keep the drop concentration invariant, then the factor becomes  $\phi^{2/3}(1-\phi)$ . Values of  $k_2$  so corrected are designated as  $k_{2,A}$  in Table 6. These values are, on balance, somewhat less constant than the  $k_{2,v}$  values.

If the intrinsic rate constants in both aqueous detergent and microemulsion are the same, the observed values differing only because of effective concentration, then the ratio of the observed second order rate constants should be given by the volume corrected values as

$$R = \frac{k_2 \text{ (micelle)}}{k_2 \text{ (m. emul.)}} = \frac{\phi_{M.E.} (1-\phi)_{M.E.}}{\phi_{micelle}} \quad (111)$$

Using the maximum values of  $k_2$  observed in aqueous CTAB (42), the experimental and calculated (equation 111) values of  $R$  are about 30 and 250, respectively. This indicates that the intrinsic rate constant in the microdroplet is an order of magnitude greater than that in the micelle. It therefore appears that the reaction in the microemulsion is taking place in an average location of lower polarity



TABLE 6. Rate constants for reaction of p-nitrophenyl diphenylphosphate with hydroxide and fluoride in a CTAB/butanol/hexadecane o/w microemulsion at 25°C (vide text)

o <sup>a</sup>	Hydroxide				Fluoride		
	k <sub>2</sub> <sup>b</sup>	k <sub>2,v</sub> <sup>c</sup>	k <sub>2,A</sub> <sup>d</sup>		k <sub>2</sub> <sup>b</sup>	k <sub>2,v</sub> <sup>c</sup>	k <sub>2,A</sub> <sup>d</sup>
0.79	2.3	1.9	1.3	-	4.1	2.8	2.4
0.70	1.5	1.2	1.1		1.7	1.5	1.3
0.58	1.1	1.1	1.1		1.2	1.2	1.1
0.47	1.0	1.0	1.0		1.0	1.0	1.0
0.36	1.0	1.9	1.1		1.1	1.0	1.1
1.25	1.2	0.9	1.1		1.4	1.0	1.3
0.16	1.8	0.9	1.4		2.0	1.1	1.6

- a) phase volume: initial composition 10% hexadecane, 90% emulsifier (50% CTAB, 50% butanol w/w).
- b) second order rate constant relative to the value at  $\phi = 0.5$  (0.13 and 0.045 M s<sup>-1</sup> for OH<sup>-</sup> and F<sup>-</sup>, respectively).
- c) each rate constant multiplied by a factor of  $\phi(1-\phi)$ ; vide text.
- d) each rate constant multiplied by a factor of  $\phi^{2/3}(1-\phi)$ ; vide text.

than in the micelle, and this effect must be more than compensating for a lower surface charge density on the microdroplet. The activation enthalpies are consistent with this view, the values for fluoride in aqueous CTAB and microemulsion ( $\phi = 0.3$ ) being about 14 and 10 kcal mol<sup>-1</sup>, respectively. In both cases, the reaction products are the expected diphenylfluorophosphonate and p-nitrophenoxide ion (equation ii).

The activation enthalpy for hydroxide is also lower in the microemulsion, but by a greater amount (14 and 8 kcal mol<sup>-1</sup> for micelle and microemulsion, respectively). It was found that the reaction produced (100%) diphenylbutylphosphate, rather than diphenylphosphate. Thus, the hydroxide produces butoxide ion in the interphase which is a more effective nucleophile. This is also consistent with studies involving replacement of CTAB with a nonionic polyoxyethylene surfactant (B200, Olin-Matheson), the results of which are shown in Figure 7. With fluoride, the rate decreases at high nonionic content as expected on the basis of decreased positive surface charge. The hydroxide decreases slightly at first, but then rises and is even higher in 100% nonionic than at 0%. We interpret this as an indication that the base is removing the proton from the terminal OH group of the surfactant, which is acting as the nucleophile. Thus, it should be possible to increase reactivity by the use of an appropriate functionalized surfactant or other suitable additive. The fact that the value of  $k_2$  for fluoride does not decrease until a high nonionic content has been reached may indicate a concomitant change in droplet size.

Finally, in connection with the use of functionalized surfactant we have performed an initial investigation in the CTAB/butanol/hexadecane microemulsion system containing 1-n-hexadecyl-3-pyridinium-aldoxine iodide (HPAI). The HPAI/CTAB ratio was 3/400. In pH 10 buffer, the second order rate constant was almost two orders of magnitude greater than in the CTAB microemulsion with no added HPAI.



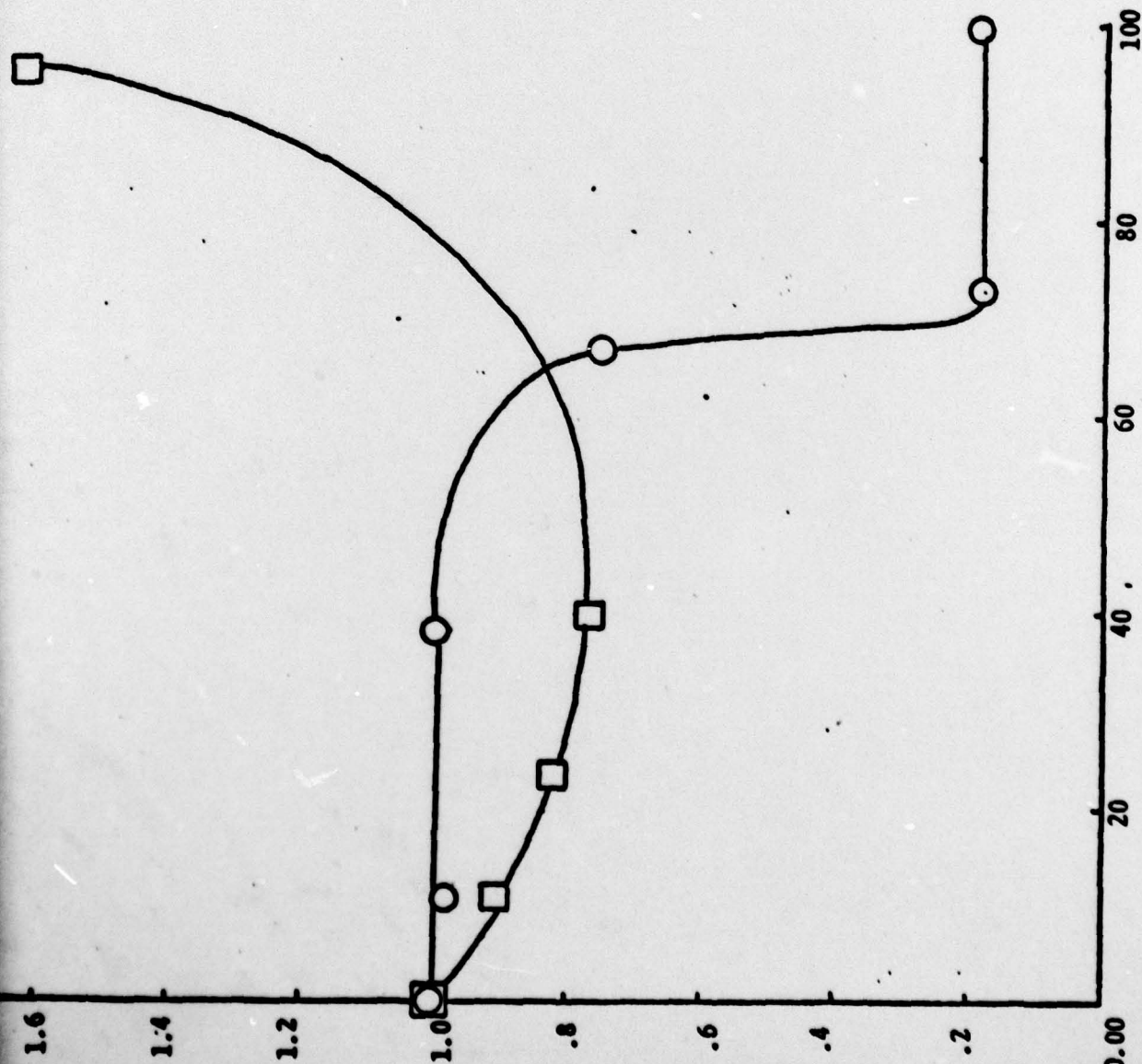


FIGURE 7 Effect of mixed CTAB/B200 microemulsions on reaction of p-nitrophenyl diphenyl phosphate with neucleophile. 1:5 mole ratio total surfactant to butanol, 10% hexadecane. Circles, F, 30% H<sub>2</sub>O, 21.5°C. Squares, OH, 40% H<sub>2</sub>O, 25.6°C.



### III. SUMMARY:

In this section are summarized some of the results and conclusions of the study. These are only meant to be used for quick reference and do not necessarily represent all of the work performed. For more complete details, the body of the report and the papers in the bibliography should be consulted.

1. A large number of oil in water microemulsions containing surfactant/alcohol emulsifier mixtures have been produced.
2. Two anionic, three cationic and nine nonionic microemulsions with mineral oil or hexadecane are reported, as well as one cationic and one nonionic system employing tributylphosphate as the oil.
3. Phase maps are available for seven microemulsion systems, one anionic, two cationic, and four nonionic.
4. Of the oils examined, tributylphosphate exhibits the largest single phase region. (CTAB/butanol system).
5. Quantitative semi-empirical relations for the transport properties of ions in nonionic microemulsions have been developed. The equivalent conductance ( $r$ ) and diffusion coefficient ( $D$ ) are related to the phase volumes ( $\phi$ ) by  $r=r_0(1-1.2\phi)^n$  and  $D=D_0(1-\phi)^{n+1}$ .
6. The value of  $n$  (above) is 1.5 at low oil content, and increases linearly with droplet diameters.
7. The droplet diameters in the nonionic systems employed here have been determined by light scattering to be in the range 80-180Å. The diameters vary exponentially with oil content.
8. Glass electrode pH measurements of aqueous buffer and microemulsion may be used to attain pH, the average of the two values. It appears that pH is related to the actual hydrogen ion activity.

9. When both forms of an indicator adsorbed by the droplet have the same average location, the intrinsic  $pK_a$  is the same in all systems of the type examined.
10. The effect of ionic strength on  $pK_a$  is negligible in ionic microemulsions and very strong in nonionic systems, corresponding to an effective dielectric constant of about 20.
11. Phosphate ester-nucleophile reactions are accelerated in cationic CTAB microemulsions. The intrinsic (phase volume corrected) second order rate constants for hydroxide or fluoride is greater in microemulsion than in aqueous CTAB micelles.
12. In phosphate ester-hydroxide reactions, the attacking species is alkoxide. In nonionic surfactant systems with a terminal hydroxyl group, this leads to rates greater than in cationic CTAB.
13. The intrinsic rate constants for the phosphate ester-nucleophile reaction are independent of phase volume.
14. Use of added functionalized surfactant leads to an additional rate enhancement of almost two orders of magnitude in CTAB microemulsion.

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